Lower Flammability Limit of Difluoromethane and Percolation Theory[1]

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Abstract

Measurements of flammability limits by the ASTM E 681 method are believed to be affected by vessel size. In order to investigate the effect of volume on measured lower flammability limits in air, the lower flammability limits of difluoromethane (R-32) at 21°C using 3 Liter, 5 Liter, 12 Liter, and 20 Liter vessels are measured. A spark ignition source is used with the voltage adjusted to the value where dielectric breakdown just begins to occur (Approximately 7 to 12 kV). The results demonstrated a higher concentration for the lower flammability limit for the 3 Liter vessel suggesting wall effects quench the flame propagation for vessels smaller than 5 Liters. The lower flammability limit for vessels with a 5 Liter or greater volume are in good agreement with those obtained in earlier investigations. For 5 Liters and larger vessels the lower flammability limit systematically shifts to higher concentrations of difluoromethane with increasing vessel size which is consistent with a percolation model. Extrapolation of the data to infinite vessel size using a percolation model yielded 15.2 percent by volume.

I. Introduction

The need to replace nonflammable chlorofluorocarbon refrigerants for protection of stratospheric ozone has raised concern about flammability of proposed alternatives. Generally if the sum of the number of C-C bonds and C-H bonds in a hydrofluorocarbon (HFC) refrigerant alternative exceeds the number of C-F bonds, one can expect the refrigerant to be flammable [1]. Marginal flammability, such as is the case for 1,1,2,2,3 pentafluoropropane (R-245ca), is expected if the number of C-F bonds equals the sum of the number of C-C bonds and C-H bonds [1]. These considerations have increased interest in

studying refrigerant flammability in recent years and has resulted in several reviews and investigations of methods used for experimental investigations [2-4].

Vapor flammability is defined as the ability to propagate a flame without limits upon initiating the flame by a spark, hot wire, or small match flame. The lower limit concentration of vapor in air where the onset of flammability begins to occur is called the lower flammability limit and the upper limit concentration of vapor in air where the initiated flame just begins to be extinguished is referred to the upper flammability limit. The ability to identify a concentration gap between a lower and upper flammability limits would mean that the vapor is flammability.

The accepted and most widely used method for experimental studies of flammability is the ASTM E 681 apparatus (See Figure 1) [5]. This method contains the vapor-air mixture inside either a 5 liter or 12 liter round bottom flask. The flame is initiated at the center of the flask by a spark, hot wire or match flame. The lower limit concentration where the flame is propagated upward into a volume generated by a 45° rotational angle measured from the vertical axis of a cone whose origin is at the center of the flask. A similar critieria is used to determine the upper flammability limit. The ASTM method also suggests types of ignition sourses (spark, hot wire and match), temperature control of the vapor air mixture, and moisture content of vapor-air mixture. Nevertheless a recent reviews have noted a significant variations [4] in flammability measurements of various workers in different laboratories[2,3]. Also differences are noted between measurements by the ASTM E 681 method and the early measurements of Coward and Jones [6], who studied upward flame propagation in a tube. In view of the variations in flammability measurements by different laboratories, an ingenious counterflow burner method has recently been proposed and developed by Womeldorf and Grosshandler [4] which is very reliable and provides for very accurate and reproducible results.

Nevertheless the question of how experimental data obtained in a small scale experiment (5 or 12 Liter flask) will carry over to the appraisal of a fire hazard in real large scale application remains [2]. In this work a percolation theory [7] is proposed to explain the effect of vessel size and the theory is used to extrapolate the lower flammability limit of R-32 to an infinite volume. The refrigerant R-32 is selected for the purpose because it has marginal flammability characteristics (i.e. high concentration for lower flammability limit) and the effect of vessel size on the lower flammability limit is greatest for such chemicals. It is the purpose of this paper to present the results of this investigation.

II. Experimental Methods and Results

The apparatus used for the lower flammability limit measurements is constructed according to the design for the ASTM E 681 method (See Figure 1). The round bottom flask containing the vapor air mixture was contained inside an insulated box with a plexiglas door to observe flask contents as shown in Figure 1. The temperature could be controlled at temperatures above room temperature using a blower which contained a heating element
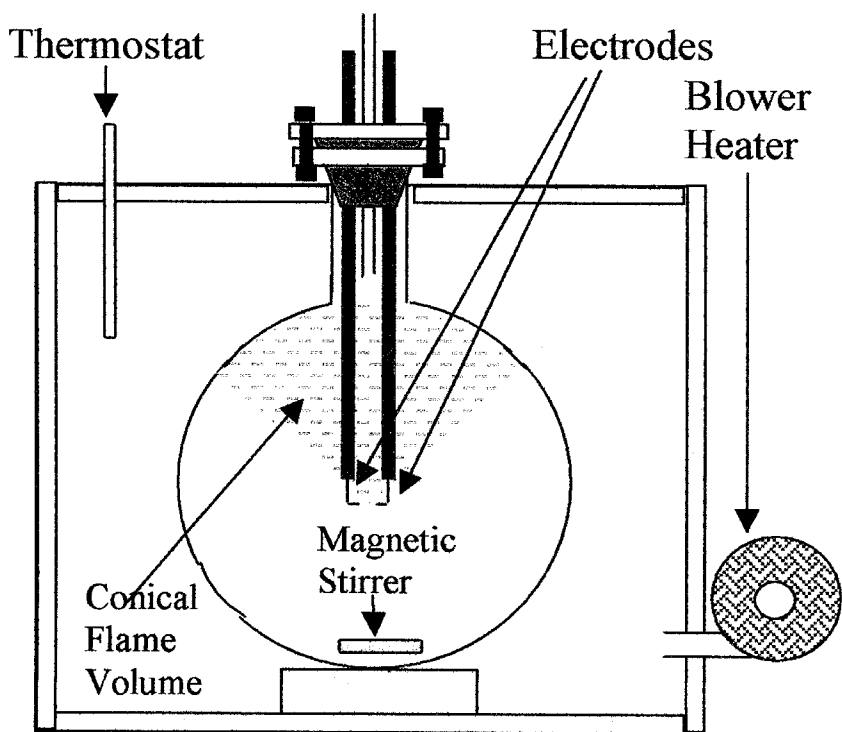
Figure 1. Sketch of the flammability apparatus.

for raising the temperature of the box above room temperature. The temperature was controlled via trimmer heater and a thermostat. Often flammability measurements are conducted at both room temperature and at 100°C. However for purposes of this work we only report results at room temperature, i.e. 21°C to within ±1°C. The temperature was measured with a thermocouple to within ±0.1°C and the exact temperature was used to calculate the molar concentration of the gases in moles/m^3 from the measured partial pressure.

The electrode assembly was held in place with a rubber stopper which also served to seal the round bottom flask. The stopper also provided entry into the flask for evacuation and introduction of gases at a desired pressure. The pressure was measured with a precision MKS capacitance pressure sensor with sensitivity of ±0.5 torr. The gases, difluoromethane and air, could be metered into the flask to a desired pressure via a needle valve. Before introducing gases the flask was evacuated to about 1 micron. After evacuation there is a 15 minute waiting period to be certain there are no leaks.

The difluoromethane used in the experiments was purchased from PCR with 98% purity and was used without further purification. Before introduction of gases, water was

first introduced into the flask via a septum, using a microsyringe, in order that the relative humidity within the flask is 50% at 21°C. The R-32 vapor is then introduced into the flask to its desired pressure (ranging from 107 to 114 torr). Lastly dry air was then introduced into the flask until the pressure was one bar. The magnetic stirrer was turned on to mix the flask contents for about 5 minutes.

To initiate the flame with a spark, a DEL high voltage power supply is used that is capable of providing voltages up to 20 kV with currents as high as 50 ma. However, the flammability experiments were conducted by adjusting the voltage and current so that the electrodes just begin to generate a spark for 0.2 to 0.4 seconds across the electrode gap of 6.4 mm. The voltage ranged from 7 kV to 12 kV depending mostly on the flask size, the larger flask size requiring the greater voltage. We also achieved great reproducibility and a very precisely defined flammability limit (to within 0.5 torr) by this procedure. This is contrary to what is recommended by ASTM E 681 method which calls for 15 kV at 30 ma. This would have been a very strong spark in our experiments and would result in considerable energy dissipation in the mixture. Such energy dissipation would place a strong perturbation on the system and ideally application of percolation theory would call for a negligible perturbation on the system by the flame initiator.

The flask and its contents were videotaped during the experiment with a Canon Video Camera and the tape could be replayed in slow motion with a VHS player. We began with a mixture concentration that was just below the flammability limit. We checked it for flammability by generating a spark. We would add R-32 to the mixture until a flame just began to propagate into the conical volume generated by rotation of a 45° conical angle as illustrated in Figure 1. This procedure would produce a final total pressure slightly above one bar by about 2 or 3 torr. We would then evacuate the flask and recharge it with the same partial pressure of R-32 and enough air to produce a total pressure of exactly 1 bar and determine if the flame propagation is reproduced. We found that the pressure or concentration for the onset of flame propagation was very reproducible. The results for the lower limit flammability is presented in units of pressure, molar concentration in moles/m^3, and volume percent for four flask sizes; with nominal volumes of 3 Liter, 5 Liter, 12 Liter and 20 Liter in Table 1. The lower flammability limit for the 3 Liter flask is much high than (about 14% higher) in the larger flasks. We interpret this to mean that the heat sink effects

Table 1

Lower Flammability limit expressed as partial pressure of difluoromethane for various flask sizes Since the total pressure is 1 bar the the partial pressure in kPa is equal to Vol% presented in the Table.

Volume (Liters)	Radius (cm)	T (°C)	Flammability (Mole/m^3)	Flammability Limit (Vol%)
3.28	9.22	22.1	6.92	15.70
5.26	10.79	20.3	5.95	14.47
12.80	14.51	21.0	6.02	14.73
21.35	17.21	22.1	6.05	14.87

of the vessel walls tends to quench the flame propagation. It is apparent from the data that one must use 5 Liter flasks and larger before vessel wall effects that quench flame propagation become insignificant.

The results for the lower flammability limit from earlier work vary from 11.5 to 15 volume percent (See Ref. [4]) for a review of results of earlier workers). For the 5 Liter flask our results (14.5%) agree very well with the hot wire ignition source 5 Liter flask results of Richard and Shankland (14.2%) and Dekleva et al. (14.5%)[3]. Good agreement for the 5 liter flask is also obtained with the very recent results of Womeldorf and Grosshandler (14.1% after conversion from equivalence rations to vol %) who used the counterflow method [4]. Generally our results yield a higher volume % for the flammability limit than earlier work (Ref. [2] 12.7% and Ref. [3] (13.9%)) in which match flame ignition sources were used.

III. Percolation Theory and Flammability Measurements

For the fundamentals of percolation theory the reader is referred to the text by Dietrich Stauffer [7]. Percolation theory is concerned with the propagation or growth of a process. It is best illustrated by considering a point lattice and picturing a fraction, p, of randomly selected points to be occupied. Connected clusters of points will be generated by connecting nearest neighbor occupied points with a bond. The value of p where the cluster size just begins to grow rapidly to infinite is referred to as the percolation limit. The bonds of the cluster may be viewed as pathways for a process, such as flame propagation, to grow and 'percolate' throughout an entire cluster.

For applications to flammability the theory has the advantage of focusing on flame propagation with a lattice model without explicitly considering the physical and chemical processes that are involved.   The physical and chemical processes would impact the parameters of the lattice model such as distance between lattice points, number of nearest neighbors, and should next nearest neighbor as well as nearest neighbor percolation be considered. However in this work we will see that effects of cluster size, i.e. vessel size, can be explained without explicitly considering the chemical and physical processes that are involved.

The vessel size determines the cluster size that is needed to provide for flame propagation throughout the vessel. The smaller the vessel, the smaller the cluster, and the lower the flammability limit concentration that is required to reach the percolation limit. The effective percolation limit, p_{eff}, for a finite size volume is related to the infinite volume percolation limit, p_c, by the power law,

$$p_c - p_{eff} \propto L^{-\frac{1}{\nu}}, \qquad\qquad (1)$$

where L is the length of one dimension of the system. The quantity, ν, is an example of a power law index which according to percolation theory is postulated to obey universality principles, i.e. is independent of the lattice details and is dependent at most the dimension

and symmetry of the system. The parameter, ν, is the power law index for the correlation length and its value has been calculated to be 4/3 for a 2 dimensional system and 0.9 for a three dimensional system [7].

The fraction of occupied sites may be regarded as proportional to molar concentration, ρ, of a real system by simple change of length scales. Thus we rewrite the above relation in terms of ρ_{eff} and ρ_c as,

$$\rho_{eff} = \rho_c - AL^{-\frac{1}{\nu}} , \qquad\qquad (2)$$

where the change in length scale has been lumped into the proportionality factor A. In modeling flame propagation, ρ_c would correspond to the flammability limit for an infinite
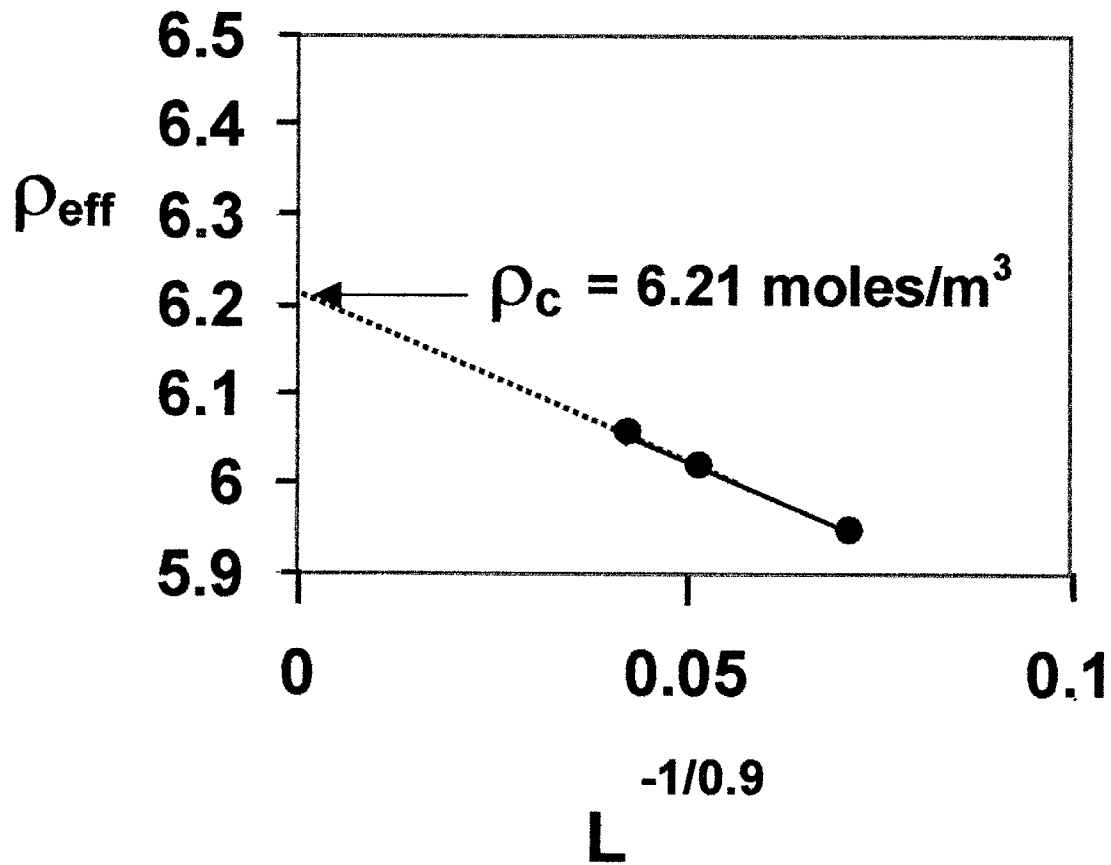

Figure 2. Plot of the molar density versus $L^{-\frac{1}{\nu}}$ for a 3 dimensional flame propagation. Experimental results are given as ● whereas the lines represent results of a linear least squares fit.

vessel volume.   The proportionality factor A is dependent on the lattice and therefore would embody the detailed physical and chemical aspects of the percolation process which in our case is flame propagation.

Figure 2 provides a plot of ρ_{eff} versus $L^{-\frac{1}{\nu}}$ where we set ν equal to its three dimensional value of 0.9. The L is assigned the value of the radius of the flask in cm given in Table 1.   The intercept, $\rho_c = 6.21$ moles/m^3, obtained from a linear least squares fit represents the flammability limit for an infinite volume. This is equivalent to 15.2% by volume. The data for the 3 Liter flask ($\rho_{eff} = 6.93$ moles/m^3) would be off the scale of the graph and was excluded from the least squares calculation because we concluded that the vessel walls affected the three Liter flask results.

IV. Conclusions

The percolation theory is useful to account for volume effects on the lower flammability limit measurements by the ASTM methods, for flask volumes of 5 Liters or more.   This is consistent with previous results and is consistent with the practice when using the ASTM methods.   The volume effect is small for flask volumes of 5 Liters or more, but nevertheless significant, the infinite volume limit being 15.2 % by volume as compared with 14.5% by volume for the 5 Liter flask.

Since the flame propagation is directed upward, the model for flammability is directed percolation rather than isotropic percolation. Consequently the value for ν may be intermediate between the value for 3-dimensions, 0.9 (used in our calculations), and the value for 2-dimensions, 1.3333.   Lattice methods for percolation processes can be used to investigate if the 3-D value of ν is appropriate and may yield a better value for ν [8].   We would point out that the extrapolation to the infinite volume flammability limit is not very sensitive to ν and the extrapolation method should still be useful for the 3-dimensional value of ν. Also in this work we suggest using minimal voltage and current settings to generate a spark, because minimal perturbation on the system to initiate the flame is consistent with percolation theory approach. This method also provided for excellent reproducibility of the flammability measurements. Reexamination of the ν value and the effect of voltage and current settings were beyond the scope of this work and these are reserved for future investigations.

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